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DETERMINATION OF PYRIDINE IN MODIFIED JP-4 VIA HIGH PERFORMANCE--ETC(U)
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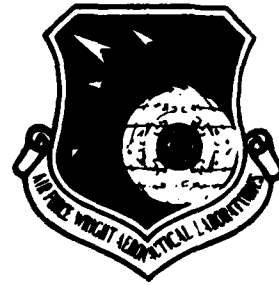
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DETERMINATION OF PYRIDINE IN MODIFIED JP-4 VIA
HIGH PERFORMANCE LIQUID CHROMATOGRAPHY (HPLC)

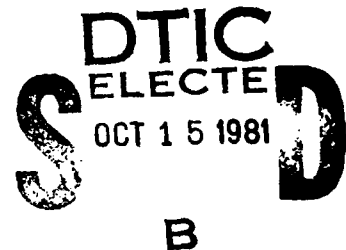
Paul C. Hayes, Jr.

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Fuels and Lubrication Division

April 1981

TECHNICAL REPORT AFWAL-TR-80-2081

Final Report for Period June 1975 - July 1975



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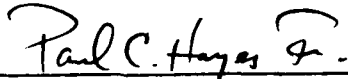
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This technical report has been reviewed and is approved for publication.



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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER AFWAL-TR-80-2081	2. GOVT ACCESSION NO. AD A105589	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) DETERMINATION OF PYRIDINE IN MODIFIED JP-4 VIA HIGH PERFORMANCE LIQUID CHROMATOGRAPHY (HPLC).		5. TYPE OF REPORT & PERIOD COVERED Final Report June - July 1975
6. PERFORMING ORG. REPORT NUMBER		7. AUTHOR(s) Paul C. Hayes Jr.
8. CONTRACT OR GRANT NUMBER(s)		9. PERFORMING ORGANIZATION NAME AND ADDRESS Aero Propulsion Laboratory (AFWAL/POSF) AF Wright Aeronautical Laboratories Wright-Patterson AFB Ohio 45433
10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS P.E.: 62203F Task: 304805 Work Unit: 30480591		11. CONTROLLING OFFICE NAME AND ADDRESS Aero Propulsion Laboratory (AFWAL/POS) AF Wright Aeronautical Laboratories Wright-Patterson AFB Ohio 45433
12. REPORT DATE April 1981		13. NUMBER OF PAGES 23
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		15. SECURITY CLASS. (of this report) Unclassified
16. DISTRIBUTION STATEMENT (of this Report) Approved for public release; distribution unlimited.		15a. DECLASSIFICATION DOWNGRADING SCHEDULE
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Pyridine High Performance Liquid Chromatography Ultra-Violet Detector Bonded Phase Chromatography		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) A study was initiated to accurately determine the weight percent of pyridine present in pyridine-modified JP-4 used for contractual combustion studies. High Performance Liquid Chromatography (HPLC) was the method of choice. A chromatographic process was developed and systematic quantitative analyses performed to substantiate the accuracy and precision of the new test method. A computing integrator interfaced with the HPLC system performed all data collection and calculations automatically, with the results printed on a		

Block 20. Abstract

teletype. Least square curve fitting accentuated the reliability for determining pyridine in the 0.5 to 5.0 weight percent concentration range.

FOREWORD

This technical report describes work performed under the In-House Project Number 3048, Task Number 304805, Work Unit number 30480591, administered by the Fuels Branch (POSF), Fuels and Lubrication Division (POS), Aero Propulsion Laboratory (APL) of the Air Force Wright Aeronautical Laboratories. Project scientist for this program was Mr. Paul C. Hayes, Jr. This report was prepared by Mr. Hayes.

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LIST OF ABBREVIATIONS

ABBREVIATION	MEANING
HPLC	<u>H</u> igh <u>P</u> erformance <u>L</u> iquid <u>C</u> hromatography
ml	millilitres
min	minute(s)
mm	millimetres
cm	centimetres
n'	effective theoretical plates
RT'	component's adjusted retention time
PW	component's corresponding peak width in time
KF	calibration factor
I.S.	internal standard
C.S.	calibration standards
U.S.	unknown sample
JP-4	jet propulsion fuel, wide-boiling range, conforming to MIL-T-5624

SECTION I

INTRODUCTION

The experimental study detailed in this technical report is one of many potentially useful applications of High Performance Liquid Chromatography (HPLC) in the determination of various additives and constituents in hydrocarbon fuels as well as different lubrication oils. The purpose of this effort was to accurately analyze three fuel samples of conventional JP-4 fuel that had been artificially doped with 0.5 to 5.0 weight percent levels of pyridine. These pyridine-modified fuels represented jet fuel with a high nitrogen content. A rapid, in-house method of analysis was desired to monitor the blending of several thousand gallons of fuel. The primary task, consequently, was to develop a 15-minute HPLC method to detect pyridine and quantitate via the most accurate technique available, i.e. internal standardization.

The analytical technique of chromatography is one of the most powerful methodologies ever developed. Nearly every analytical laboratory in the world utilized some form of chromatographic instrumentation (see Reference 1.) Liquid Chromatography has been understood in principle for at least 55 years, but not until the last decade have suitable high pressure pumps and sensitive, low dead volume detectors been commercially available. Most materials have the ability to absorb some radiation at the ultraviolet wavelengths. Particularly intense absorbers are the aromatic molecules; thus, the ultraviolet detector is used widely in HPLC to determine aromatic species, e.g. pyridine in this study.

Chromatography is a separation technique which fractionates a sample and then measures or identifies the fractions in some way. The heart of any chromatographic system is the column. The liquid chromatographic column contains a stationary phase which in the case of this study was chemically bonded to solid inert material called the support. The sample to be analyzed is injected into the column and moves across or through the stationary phase, being pushed along

by the liquid mobile phase. In the form of liquid chromatography utilized in this report, the various components in the injected sample were separated according to their degree of solubility in the stationary phase. Simply, "like dissolves like." For a polar, bonded phase column, polar compounds such as pyridine were held or retained in the polar stationary phase longer than the relatively less polar aromatic hydrocarbons in the fuel matrix. Thus a separation was effected between the pyridine and the less polar aromatics and, for that matter, the even less polar saturated and olefinic hydrocarbons. The almost insoluble fuel matrix was hardly delayed at all--essentially, it did not notice the presence of the stationary phase and passed through the column at almost the speed of the mobile liquid phase. The more soluble pyridine was retained considerably longer until enough solvent had passed through the column to bring the component to the end and emerge or elute. The pyridine was then detected and quantitated by the ultraviolet detector stationed at the column's outlet.

SECTION II

EXPERIMENTAL APPROACH

1. INSTRUMENTATION

The basic analytical instrument utilized in this study was the Varian Model 4200 Liquid Chromatograph equipped with a fixed wavelength (254 nanometers) ultraviolet detector. All injections were performed by hand with a Shandon Model "REPRO-JECTOR" automatic syringe holder. A Spectra-Physics Model Auto-Lab System IV Computing Integrator performed the data collection and manipulations, with the calculations printed in report format at a Teletype Corporation "Teleprinter" Model ASR-33.

2. LIQUID CHROMATOGRAPHIC CONDITIONS

The HPLC Column ("Micro-Pak" NH_2) used in this work was slurry-packed by Varian Associates to the following specifications: column length of 25 centimeters, column internal diameter of 2.2 mm, and a stationary liquid phase of polymeric aliphatic amine bonded to silica gel of 10-micron nominal particle size. The optimized mobile phase composition (by volume) for this method was 90% hexane, 9.75% methylene chloride, and 0.25% iso-propyl alcohol. These solvents were the distilled-in-glass grade, used as is, from Burdick & Jackson, Inc. The flow rate of the mobile phase was 1.0 ml/min, requiring a back pressure through the column of 1950 psig. Other HPLC operating parameters were as follows:

1. Temperature of the column was maintained at 25°C via a water jacket through which distilled water was circulated and temperature controlled by a Haake Model E-52 Heater/Circulator installed in a Varian Model 4000 constant temperature bath chamber;
2. The fixed wavelength ultraviolet detector had been refabricated from copper, with the outside of the flow cell encompassed in copper tubing to enable

the detector to also be thermostatted at 25°C for greater baseline stability at high detector sensitivities;

3. electrometer on the detector was set at range, 0.005 absorbance units full scale and attenuation, 1;
4. injection volume was fixed at one-half a microliter;
5. column conditioned prior to usage to remove interfering polar aromatic impurities at a flow rate of 2.0 ml/min for 4 hours with iso-propyl alcohol and reconditioned for another 4 hours at the same flow rate with the mobile phase composition cited above for the analysis (column outlet unattached).

One measure of column efficiency is its number of theoretical plates, a concept derived from distillation theory; the greater the number, the more able is the column to resolve components of similar polarity. The theoretical plates were determined to be nearly 1000, comparable to most of the high-pressure liquid chromatographic columns commercially available at the time of this report. The equation used for measuring a column's effective theoretical plates (n') was:

$$n' = 16.0 \frac{(RT')^2}{(PW)}$$

- a) where RT' = the adjusted retention time, i.e. absolute retention time minus column dead volume time (i.e. unretained toluene here);
- b) and PW = peak width, i.e. the portion of the peak's baseline intersected by tangent's drawn to the peak's sides (time units).

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The sample analyzed to determine column efficiency was a one-microliter injection of naphthalene, o- and m-nitroaniline dissolved in hexane and run at ambient conditions in a mobile phase consisting of 75 percent hexane, 24.5 percent methylene chloride, and 0.5 percent iso-propyl alcohol at a flow rate of 1.67 ml/min.

SECTION III

QUANTITATION

1. BACKGROUND

The most accurate method of quantitating component concentrations in liquid chromatography is by internal standardization (Reference 2). This method applies normalized calibration or response factors to each peak area accumulated by the integrator from the detector's electrometer and calculates the concentration of each component in the analysis sample. The internal standard is assumed to have a calibration factor of 1.000.

Both apparatus and procedural errors can be eliminated by the addition of an internal reference standard to the unknown sample. If the internal standard is introduced before the chromatographic process, it may also compensate for errors during the preparation of the sample. The requirements, however, for the employment of the internal standard are rather stringent:

1. It must be completely resolved.
2. It must elute near the peak(s) of interest.
3. It must be similar in concentration to the peak(s) of interest.
4. It must be chemically inert.
5. It must be absent in the original unknown sample.

After trial and error, a suitable internal standard was found in diethyldiphenylurea, research grade, purchased from Pfaltz & Bauer, Inc. This compound eluted between the unretained aromatic and saturated hydrocarbons and the component of interest, pyridine (see Figure 1). Furthermore, after chromatographic runs on pyridine solutions of approximately the weight percent anticipated, it was decided that a dilution factor of ten should be employed for all samples to ensure baseline resolution of all peaks of interest. No pyridine was detected in the original JP-4 base stock.

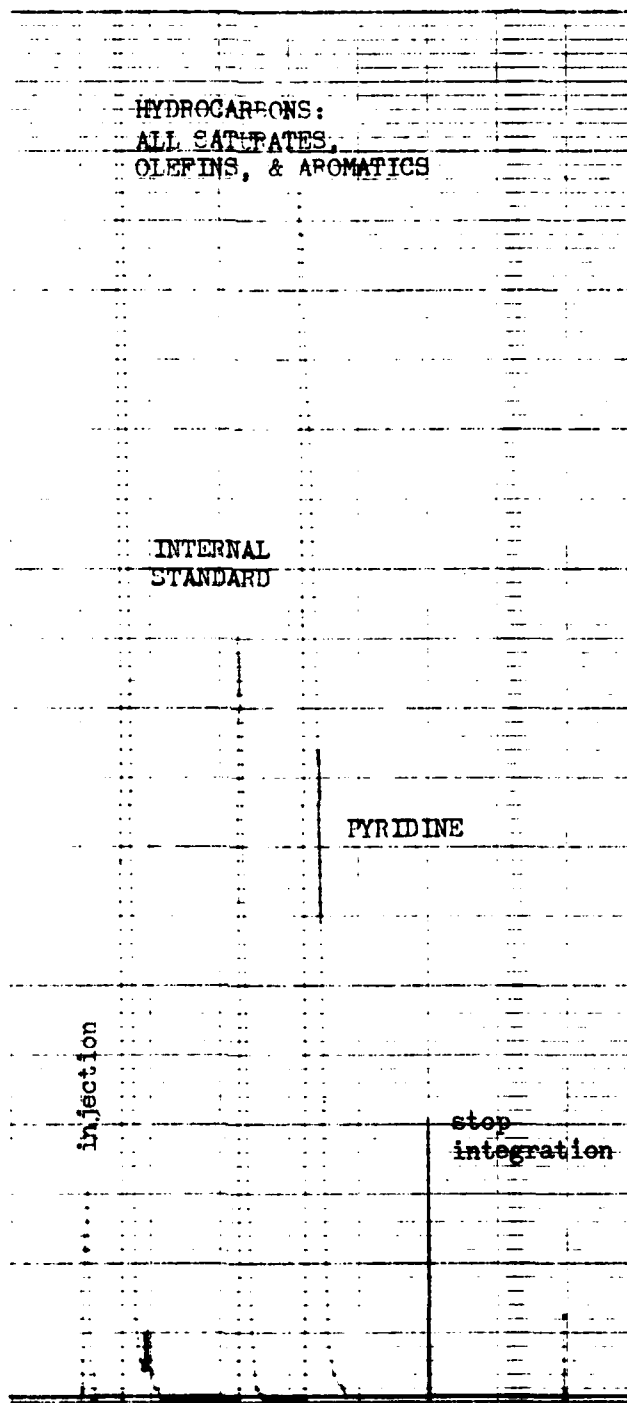


Figure 1. Typical HPLC Run On Pyridine-Modified JP-4 Fuel

All calculations were performed automatically by the Auto-Lab Computing Integrator. Pyridine was identified by relative retention time (relative to the internal standard) and the correct calibration factor (KF) applied to the peak area. In this way, the internal standard peak was used as both the retention time and calibration factor reference point. The calculations (by weight) of the pyridine were automatically performed using Equation 1:

$$\text{weight \% Pyridine} = \frac{(\text{AREA}_{\text{pyr}}) (\text{KF}_{\text{pyr}}) (\text{AMT}_{\text{is}})}{(\text{AREA}_{\text{is}}) (\text{AMT}_{\text{sam}})} \quad (1)$$

where AREA_{pyr} = the integrated peak area of pyridine

KF_{pyr} = the calibration factor for pyridine

AMT_{is} = the weight of internal standard in the unknown sample

AREA_{is} = the integrated peak area of the internal standard

AMT_{sam} = the weight of analysis sample used in the prepared sample

2. CALIBRATION STANDARDS

Approximately 1 gram of the internal standard (I.S.) was accurately weighed and the amount recorded. The I.S. was then washed into an amber 100-ml volumetric flask and diluted to the calibration mark with JP-4. Other volumetric flasks were weighed with their stoppers and recorded. To prepare diluted pyridine concentrations in the range of 0.05 to 0.50 weight percent, approximately 0.05, 0.10, and 0.50 grams of pyridine were accurately weighed into each volumetric flask and diluted with 50 ml of JP-4. A 10-ml aliquot of the internal standard solution was then added to each flask. The flasks were diluted to the mark with JP-4, re-stoppered, and accurately reweighed.

Table 1 summarizes these weighings and displays the calculated weight percentages of both pyridine and the diethyldiphenylurea for the calibration standards.

TABLE 1
CALIBRATION STANDARDS (C.S.) PREPARATION

C.S. CODE I.D.	TOTAL WEIGHT FLASK & FUEL (grams)	WEIGHT EMPTY FLASK (grams)	WEIGHT FUEL (grams)	WEIGHT PYRIDINE (grams)	WEIGHT % PYRIDINE PRESENT	WEIGHT I.S. in ALIQUOT (grams)	WEIGHT % AREA PRESENT
DL-S	136.8486	61.2746	75.5740	0.0471	0.06232	0.10014	0.1325
DM-S	141.0377	65.5483	75.4894	0.0994	0.13167	0.10014	0.1326
DH-S	135.7087	60.0746	75.6341	0.5297	0.70035	0.10014	0.1324

Multiple liquid chromatographic runs were made on the above calibration standards. An average calibration factor for pyridine, relative to the internal standard, could then be derived using quantities listed in Table 1, the appropriate peak areas and Equation 1. This calibration factor, applicable to anticipated pyridine concentrations (diluted) in the range of approximately 0.05 to 0.70 weight percent was 1.608 for 25 determinations with a standard deviation of 0.078.

To check the accuracy of this calibration factor, the above calibration solutions were back-analyzed, i.e. treated as unknown samples (that had already been diluted). These data are presented in Table 2. Figure 2 is a least-squares plot relating known concentration of pyridine in the calibration standards to the found concentrations. The excellent accuracy possible for pyridine determination employing the above calibration factor was reflected in the near unity correlation coefficient of 0.9999953 and the low standard error of estimate of 0.001115.

TABLE 2
BACK-ANALYSIS RESULTS ON CALIBRATION STANDARDS
FOR PYRIDINE CONTENT

<u>C.S. CODE I.D.</u>	<u>KNOWN WEIGHT % PYRIDINE</u>	<u>FOUND WEIGHT % PYRIDINE</u>	<u>STANDARD DEVIATION OF DETERMINATIONS</u>	<u>RELATIVE STANDARD DEVIATION (%) OF DETERMINATIONS</u>
DL-S	0.0623	0.0595	0.0014	2.35
DM-S	0.1317	0.1329	0.0013	0.98
DH-S	0.7004	0.7206	0.0070	0.97

3. UNKNOWN SAMPLES

Unknown samples were treated in the following manner. Exactly 10 mls of the unknown samples were pipetted into a pre-weighed volumetric flask and the flasks were reweighed. Table 3 shows the final weights of unknown samples in the respective flasks. Before being chromatographed, the sample was diluted with 50 ml of JP-4, a 10-ml aliquot of the internal standard was then added, and the flask re-weighed after dilution to the 100-ml mark with JP-4.

TABLE 3
UNKNOWN SAMPLE (U.S.) PREPARATION

<u>U.S. CODE I.D.</u>	<u>TOTAL WEIGHT FLASK & SAMPLE (grams)</u>	<u>WEIGHT EMPTY FLASK (grams)</u>	<u>WEIGHT SAMPLE PRESENT (grams)</u>
DEL-F-4-S	48.5725	40.8578	7.7147
DEL-F-5-S	75.0919	67.4225	7.6694
DEL-F-5-S	70.5179	62.8508	7.6671

The above aliquot and weight information along with the calibration factor previously derived were entered into the memory of the Auto-Lab Computing Integrator. The unknown solutions were then repeatedly

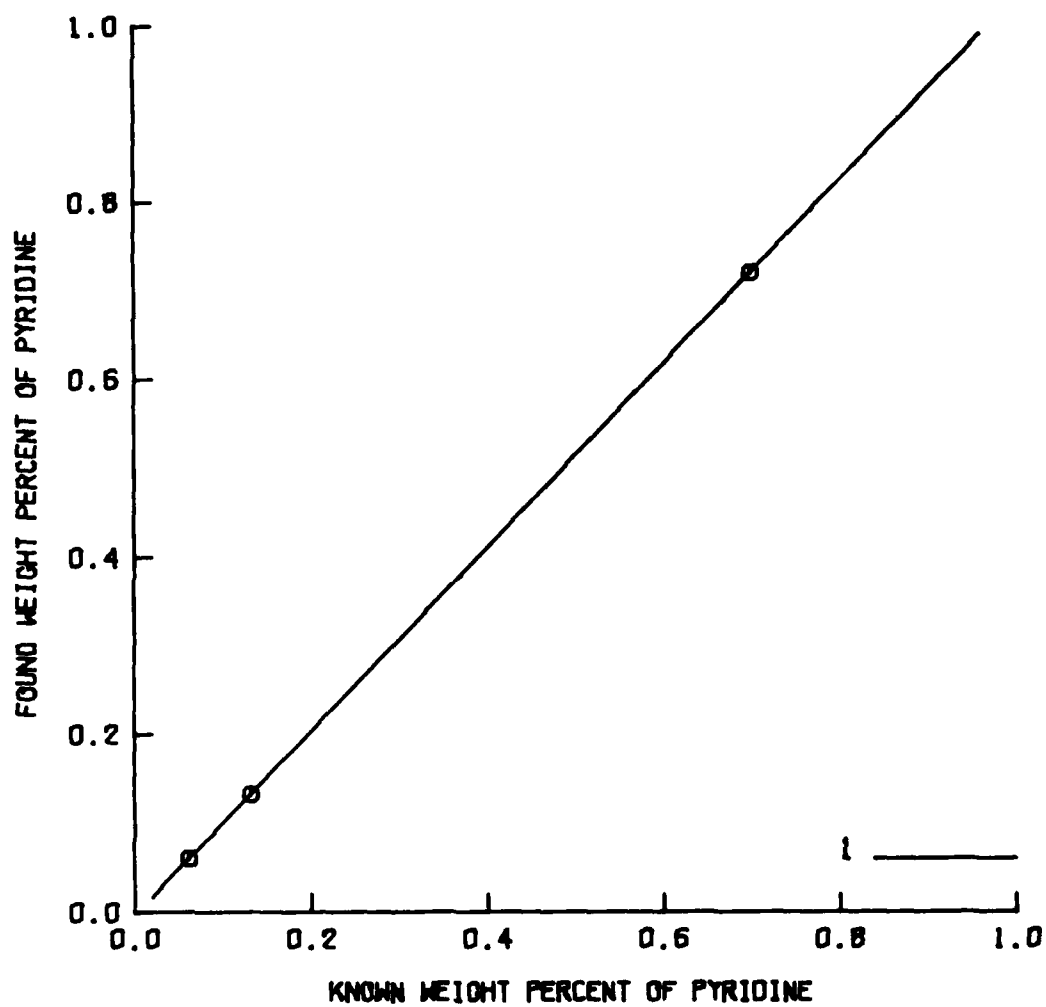


Figure 2. Back-Analysis Of Calibration Standards

chromatographed; the Auto-Lab calculating the pyridine content automatically via Equation 1. These results are displayed in Table 4.

TABLE 4
ANALYSIS OF UNKNOWN SAMPLES (U.S.) FOR PYRIDINE CONTENT

<u>U.S. CODE I.D.</u>	<u>FOUND WEIGHT % PYRIDINE</u>	<u>STANDARD DEVIATION OF DETERMINATIONS</u>	<u>RELATIVE STANDARD DEVIATION (%) OF DETERMINATIONS</u>
DEL-F-4	6.032	0.045	0.75
DEL-F-5	1.687	0.014	0.83
DEL-F-6	0.627	0.012	1.91

Please note the low relative standard deviations for the repeat determinations and that these deviations correspond in magnitude with the previously discussed results on the back-analyzed calibration standards. It was subsequently discovered that the actual weight percentages of pyridine measured into the above unknown modified fuel samples was almost exactly what this method predicted.

SECTION IV

CONCLUSIONS

1. High Performance Liquid Chromatography, i.e. HPLC, has demonstrated excellent accuracy and repeatability in determining pyridine in pyridine-modified JP-4.
2. The entire chromatographic process was complete in less than 15 minutes.
3. A high degree of accuracy and precision was accomplished through the internal standardization method of quantitation.
4. The Auto-Lab System IV Computing Integrator performed all data collection and internal standardization calculations automatically, with the results printed on a remote teletype.

SECTION V

FUTURE WORK

1. High Performance Liquid Chromatography, i.e. HPLC, will be a powerfully selective tool for the qualitative identification and quantitative determination of selected aromatic fuel constituents.
2. Complete automation of the HPLC system, i.e. sample injection via a closed loop initiated by a controlling unit such as the Auto-Lab System IV Computing Integrator, will realize considerable savings in technician time for unattended analyses and substantially improve repeatability of the determinations.

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1. Herbert L. Kahn and Zane Bitterfield, "HPLC-A Sleeping Giant," Industrial Research, June, 1973, pp. 32-35.
2. Fred Baumann, Basic Liquid Chromatography, 1972, Varian Aerograph, Chapter 8, pp. 8-12 through 8-16.

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